SORPTION OF SUPERCRITICAL CARBON DIOXIDE BY SOME POLYMERS: IN SITU INVESTIGATION

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INTRODUCTION

A convenient optical method for investigation of CO_2 diffusivity in polymers under sorption in supercritical conditions was employed in [1]. However, successful implementation of this technique requires detailed study of the optical boundaries formation in polymers. In present work we have developed the explanation of the optical boundaries formation in poly(methyl methacrylate) (PMMA) and poly(butyl methacrylate) (PBMA) samples during sorption in supercritical CO_2. The realized approach is based on experimental results and computer simulation. The different models for the dependence of diffusion coefficient of CO_2 on the concentration of CO_2 in a polymer were suggested for PMMA and PBMA.

MATERIALS AND METHODS

Experiments with supercritical CO_2 were made using the special cuvette, which was designed on the basis of one described earlier [1]. A polymer sample as a parallelepiped with an edge length of 1-5 mm was mounted in the cuvette, which was sealed, and temperature was elevated to a prescribed value. Then, by increasing the syringe pressure, supercritical CO_2 was allowed into the cuvette and the sample was observed with a video camera through the cuvette optical channel. This experimental scheme made it possible to study the kinetics of changes in linear dimensions of polymer samples in the supercritical fluid and to monitor the propagation of optical boundaries. The polymeric materials used had the following characteristics - PBMA: M_w = 2236000, M_n = 861400, M_w/M_n =2.6 (as determined with GPC), r=1070 kg/m^3, T_g=27°C; PMMA: M_w = 4098000, M_n =2530400, M_w/M_n = 1.6 (GPC), r=1170 kg/m^3, T_g=114°C. Carbon dioxide of high purity grade (>99.997%, O_2 0.0002%, H_2O 0.001%) was used as received.

RESULTS AND DISCUSSION

Formation and Movement of Optical Boundaries in Samples

We applied an optical method for determination of diffusion coefficients by analyzing the kinetics of motion of the optical boundaries formed in an optically transparent sample under sorption in supercritical fluid conditions. Figure 1 shows the photographs of the stages of CO_2 sorption by the polymers as taken with an optical microscope. It is seen that a distinct optical boundary (dark, relatively narrow band) is formed in the PMMA sample (Fig. 1A), which moves (as CO_2 is absorbed) from the surface to the center of the sample. The sample regions on both sides of the boundary are substantially lighter as compared to the boundary. In this case, the motion of the optical boundary can be monitored up to its contraction in the center. The picture observed for PBMA (Fig. 1B) is somewhat different. Here are darkened areas characterized by sharp boundaries that also move to the sample center; reaching the central region of the sample, the boundary becomes hardly distinguishable. The entire region

between the optical and physical boundaries of the sample appears to be substantially darker than the central region. This effect is especially pronounced in the initial sorption step; further, the darkened areas gradually become lighter. The typical time curves for motion of optical boundaries in PMMA and PBMA samples are presented in Fig. 2a. To measure the distance travelled by a boundary, the sample center was taken as a reference point. It is seen that the square distance covered as a function of time can be approximated with good accuracy by a straight line for both polymers. It is known that, if the diffusion coefficient is invariable, the initial concentration distribution in a sample smoothes with time: the characteristic sizes of regions with significant gradient of concentration increase. In the case
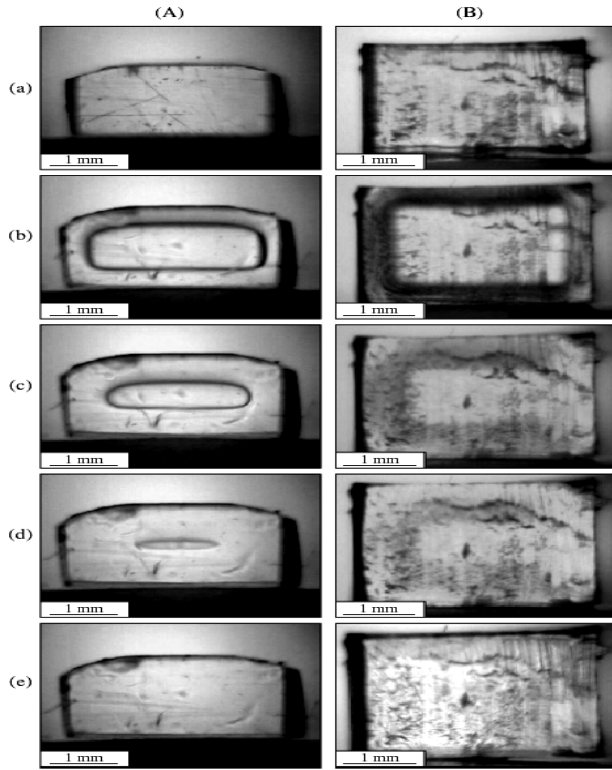
of sorption, the concentration gradient is described by Gaussian curves with a maximum at the physical boundary of the sample and the width increasing proportionally to $t^{1/2}$. If the refractive index depends on the sorbate concentration, it is possible that darkened areas with a sharp transition region (optical boundary) will be formed in a sorbing sample, but the width of the transition region will increase with time proportionally to $t^{1/2}$ and the optical boundary will smear. Since sharp, moving optical boundaries without diffusional smearing are observed in the samples (Fig. 1), the mechanism of their formation should be interpreted in terms of the assumption of a pronounced concentration dependence of the CO_2 diffusion coefficient in PMMA and PBMA.

Figure 1. Steps of CO_2 sorption by PMMA (A) and PBMA(B) samples during exposure under supercritical conditions at temperature 38°C and pressure 12.5 MPa. Exposure time for (A): (a) 0, (b) 20, (c) 40, (d) 60, and (e) 80 min and for (B): (a) 0, (b) 2, (c) 4, (d) 6, and (e) 8 min.

Formation of the Optical Boundaries in PMMA Samples

We propose the following model to explain the formation of the optical boundary in the case of PMMA. Since the experiments were made at a temperature below the Tg of PMMA, the sample placed in supercritical CO_2 initially occurred in the glassy state. Further, with the progress of CO_2 sorption, the polymer, as a rule, undergoes a transition to the elastic state. It may be assumed that the transition takes place in each region of the sample upon exceeding the local concentration of absorbed CO_2 over a certain limiting value C_x. Let us also assume that the diffusion coefficients of CO_2 in the elastic polymer, D_1, and in the glassy polymer, D_2, are different, being $D_1>D_2$ (in the simplest case, it may be assumed that D_1 and D_2 do not depend on concentration). Thus, the simplest pattern of diffusivity in PMMA is as follows:

$$D(C) = \begin{cases} D_1 = const & C > C_x \\ D_2 = const & C < C_x \end{cases} \quad D_1 > D_2 \qquad (1)$$

Then, the analysis reduces to the well-known Stefan problem [2, 3], whose solution (the Neumann solution for a semi-infinite medium) predicts a linear relation between the squared displacement of the front of constant concentration C_x and time:

$$X^2 = \alpha D_1 t \tag{2}$$

The dimensionless proportionality factor α in this case is a root of the equation:

$$\frac{\frac{C_x}{C_0} - 1}{erf\left(\frac{\sqrt{a}}{2}\right)} e^{\frac{-a}{4}} + \frac{\frac{C_x}{C_0}}{\sqrt{\frac{D_1}{D_2}}\left(1 - erf\left(\frac{\sqrt{a}}{2}\frac{D_1}{D_2}\right)\right)} e^{\frac{-a}{4}\frac{D_1}{D_2}} = 0 \tag{3}$$

where erf(x) is the error function and c_0 is the CO_2 concentration at the physical boundary of a polymer. Thus, the α value is uniquely determined by two ratios D_1/D_2 and C_x/C_0. The region of the propagating front of constant concentration C_x is characterized by a finite jump in the concentration gradient, whose value is defined by the relationship:

$$D_1 \frac{dC_1}{dx} = D_2 \frac{dC_2}{dx} \tag{4}$$

where C_2 and C_1 are the concentrations ahead of and behind the front, respectively. From Eq. (4), it is seen that the concentration gradient in the region immediately before the front is dominates when D_1 and D_2 are considerably different. If the refractive index is concentration dependent, this leads to the formation of an optical boundary in this region [4, 5]. The angular deviation of a light beam propagating in an optically nonuniform system over a small distance dz is defined by [6]:

$$da = \frac{|\nabla_\perp n|}{n} dz \tag{5}$$

where $\nabla_\perp n$ is the projection of the refractive index gradient onto the direction of the principal normal to the beam trajectory. Beams passing near and parallel to the front of constant concentration C_x will substantially deviate, producing a darkened area on the sample image. Such darkened areas will be localized only in a rather narrow region immediately before the front, where the corresponding component of concentration gradient has a significant value according to Eq. (4). Then, the forming optical boundary will appear as a relatively narrow dark band, as we find in PMMA samples (Fig. 1A). Therefore, we assume that Eq. (1) is a good approximation for the actual concentration dependence of the diffusion coefficient in PMMA. The movement of an optical boundary will be determined by the propagation of the front of constant concentration C_x and, for this reason, must obey relationship (2), which is observed in the experiment (Fig. 2a). The analysis of the kinetics of the optical boundary motion allows the diffusion coefficient D_1 to be determined provided that the value of α in relationship (2) is known. In order to determine this parameter from Eq. (3), it is necessary to know the ratios C_x/C_0 and D_1/D_2. Their determination required computational simulation to be performed for fitting the experimental results.

Computer simulation. The computational modelling of the process was based on the following premises:

(1) The diffusion equation was approximated by a finite-difference scheme [7] of the first order in time (the derivative only with respect to one spatial coordinate is written in an explicit form):

$$C_{ijk}^{t+1} = C_{ijk}^t + M\left(\frac{D(C_{i+1jk}^t) + D(C_{ijk}^t)}{2}(C_{i+1jk}^t - C_{ijk}^t) - \frac{D(C_{ijk}^t) + D(C_{i-1jk}^t)}{2}(C_{ijk}^t - C_{i-1jk}^t)\right) + \ldots \tag{6}$$

where C is the normalized concentration in grid points and D is the concentration-dependent diffusion coefficient. The parameter M of the scheme was selected on the basis of the stability
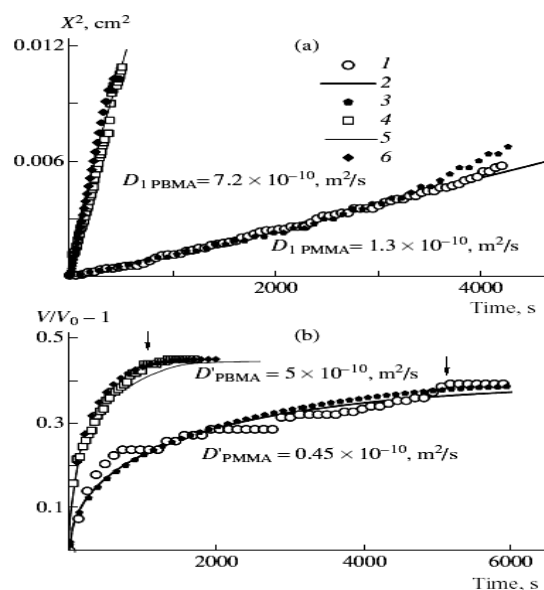
condition $MD \pounds 1/6$. The subscripts ijk and t denote grid points and time, respectively. At the initial point of time, $C_{ijk} = 0$ in all grid points, and $C_{ijk} = 1$ at any time in the boundary points.

(2) The concentration dependence of D was described in accordance with Eq. (1).

(3) The concentration dependence of the refractive index in (Eq. (5) was determined using the Lorentz–Lorenz equation [6]. The polymer refractive index $n = 1.49$ was used for both PMMA and PBMA [8] and for supercritical CO_2 the value of $n = 1.11$ at $p = 9$ MPA and $T = 42°C$ [9] was used.
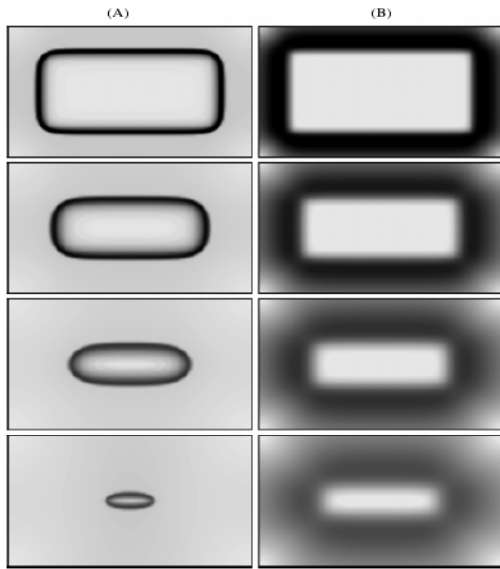
(4) The intensity loss was assumed to be proportional to the total deviation of a ray propagating in a plane-parallel beam along one of the sample axes and was calculated by numerical integration of Eq. (5).

Figure 2. Typical results obtained for propagation of optical boundaries in PMMA (_1–3_) and PBMA (_4–6_) samples and for their swelling upon exposure to supercritical CO_2 (temperature 38°C, pressure 9 MPa): (_1, 4_) experimental data; (_2, 5_) theoretical approximations of the experimental data according to Eqs. (2) and (8), respectively; (_3, 6_) computer simulation data (corresponding to the D' values calculated with Eq. (8)) for PMMA ($c_x/c_0 = 0.7$, $D_1/D_2 = 20$) and for PBMA ($D_1/D_2 = 7.5$) models. (a) Time dependence for the squared distance X^2 traveled by optical boundaries; (b) time dependence for the relative increment in sample volume (V_0 is the sample volume before swelling).

Determination of the diffusion coefficient from kinetics data on the movement of an optical boundary. The ratios C_x/C_0 and D_1/D_2 required for calculating the diffusion coefficient D_1 according to Eqs. (2) and (3) were found by the iteration procedure. For estimation of C_x/C_0, the following approach was used. Since the process of propagation of optical boundaries in PMMA can be followed up to the moment of their merging in the sample center and disappearance, it is experimentally feasible to measure the propagation time t. At the moment when the optical boundaries merge, the concentration in the center of the sample is equal to C_x. On the other hand, as known from the diffusion theory, the sorption behavior of a rectangular-shaped sample placed in a medium with a certain sorbate concentration is described by a solution to the diffusion equation with zero initial and constant boundary conditions [2, 3]. Measuring the front propagation time t (typical values are 1–1.5 h) for the known linear dimensions of samples ($\sim 2 \times 2 \times 4$ mm^3) and using the values of the apparent diffusion coefficient D' estimated by the volume swelling technique (7×10^{-11} m^2/s), we found that the typical value of the sought quantity C_x/C_0 is 0.7, $D_1/D_2 = 20$ and $\alpha = 0.7$.

The numerical experiment resulted in images of optical boundaries forming and propagating in the samples modelled (Fig. 3A); time dependence for the distance covered by an optical boundary (Fig. 2a) and calculated (by numerical integration of concentration over sample volume) time dependence of the sorbate mass (Fig. 2b). It is seen that it approximates well the experimental data and follows law (2) up to the moment of front contraction at the sample center.

Formation of Optical Boundaries in PBMA Samples

Since PBMA samples initially occurred in the elastic state (at temperatures above T_g) in the experiments, the sorption process has a somewhat different character as compared to PMMA. As has already been noted, the fact of experimental observation of propagating

optical boundaries leads to the assumption that the diffusion coefficient depends on concentration, $D = D(c)$. The shape of the optical boundary and fitting to the computational simulation results suggest that the diffusion coefficient in PBMA increases gradually (not in a jumpy manner as in PMMA) as CO_2 is absorbed. Owing to the complexity of the use of analytic procedures in solving the diffusion problem, we attempted computational simulation for fitting to the experimental data in this case as well.

Computer simulation. Modeling was based on the same premises as in the case of diffusion in PMMA, except for the assumption on the character of concentration dependence for the diffusion coefficient. As the simplest model of the function $D(c)$ for PBMA, we selected linear growth with increasing sorbate concentration:

$$D(C) = D_2 + (D_1 - D_2)C, \quad D_1 > D_2 \tag{7},$$

where c is the sorbate concentration normalized to the equilibrium value. Qualitative agreement between simulation results and the experimental data was achieved by varying D_1/D_2. Such an analysis allowed the suggestion to be made that the D_1/D_2 ratio for PBMA lies in the range 5–10. Under these conditions, the images obtained by computational simulation have darkened areas with a relatively sharp boundary (Fig. 3B) which qualitatively resemble those observed experimentally (Fig. 1B). Numerical analysis shows that the boundary propagation law in this case (as a reference, we took the point at which the intensity of darkening is half its maximum value, as in the real experiment) also has the form defined by Eq. (2) (Fig. 2a). The sorbate concentration in the boundary region turned out to be 2–4% of the equilibrium value. The factor $\alpha \approx 3$ (at $D_1/D_2 \approx 7$ or greater) was determined; this value we used to calculate the coefficient D_1 in PBMA from the experimental data using Eq. (2).

Figure 3. Results of computer simulation of the processes of formation and propagation of optical boundaries in polymer samples for (A) the PMMA model (Eq. (1)) at $c_x/c_0 = 0.7$ and $D_1/D_2 = 20$ and (B) the PBMA model (Eq. (7)) at $D_1/D_2 = 7.5$. The images for each set were calculated in equal time intervals.

Analysis of Volume Swelling Kinetics

The values obtained for D_1 were compared with the results of the analysis of the volume swelling kinetics. From Fig. 1, it is seen that the linear dimensions of samples increase during their exposure to supercritical CO_2. Our scheme used to monitor the swelling of a sample in supercritical CO_2 makes it possible to measure growth in two linear dimensions. On the basis of these measurements, we drew conclusions on the dynamics of a gain in sample volume. Let us assume, volume changes to be proportional to the mass of absorbed CO_2. The exact solution for the time dependence of the sorbate mass in a sample at zero initial and constant boundary conditions is as follows [2, 3]:

$$\frac{M(t)}{M_\infty} = 1 - \frac{512}{p^6} \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp\left(-\frac{p^2(2i+1)^2 D't}{l_x^2}\right) \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2} \exp\left(-\frac{p^2(2j+1)^2 D't}{l_y^2}\right) \times$$
$$\times \sum_{k=0}^{\infty} \frac{1}{(2k+1)^2} \exp\left(-\frac{p^2(2k+1)^2 D't}{l_z^2}\right) \tag{8},$$

Table 1. Equilibrium swelling degrees and CO_2 diffusion coefficients in PBMA and PMMA as measured at a fixed temperature (38°C) and different pressures

Polymer	Pressure, MPa	$D_1 \times 10^{-10}$, m²/s	$D' \times 10^{-10}$, m²/s	Degree of swelling, vol %
PBMA	9	5.1 ± 0.2	5.8 ± 0.7	49 ± 8
	12.5	6.5 ± 0.5	4.4 ± 0.4	46 ± 7
	15	4.8 ± 1.0	4.4 ± 0.4	47 ± 10
PMMA	9	1.04 ± 0.10	0.51 ± 0.08	24 ± 5
	12.5	1.35 ± 0.12	0.69 ± 0.09	26 ± 8
	15	2.0 ± 0.30	0.7 ± 0.30	37 ± 5

where $M(t)$ is the sorbate mass, M_μ is the equilibrium mass of the sorbate, and D' is the diffusion coefficient. This equation is valid at $D' = \text{const}$. However, as shown by the numerical experiment (Fig. 2b), Eq. (8) also satisfactorily approximates the calculated functions $M(t)$ with the concentration-dependent diffusion coefficient as defined by Eq. (1) or (2). In this case, the diffusion coefficient D' should be considered as an apparent quantity characterizing the rate of sorption by the sample as a whole. Table 1 presents the data of equilibrium swelling degrees and CO_2 diffusion coefficients for PMMA and PBMA.

CONCLUSIONS

Based on the analysis of the movement of optical boundaries and the kinetics of swelling, the diffusion coefficients of CO_2 in the polymers were obtained. The equilibrium degrees of swelling were determined. According to the model proposed for PMMA, the diffusion coefficient increases dramatically, by more than an order of magnitude, when the sorbate concentration reaches a certain limit (~70% of the equilibrium value). We assume that the polymer undergoes a transition from the glassy to the elastic state at this concentration of CO_2 absorbed under the given experimental conditions. For PBMA, the diffusion coefficient is supposed to increase gradually (5–10 times in total), thus resulting in the development of an optical boundary of another form than in the case of PMMA.

REFERENCES:

[1] NIKITIN, L., et al. Macromolecules, Vol. 35, **2002**, p. 934

[2] CARSLAW, H.S., JAEGER, J.C., *Conduction of Heat in Solids*, Oxford: Clarendon, 1959.

[3] CRANK, J., *The Mathematics of Diffusion*, Oxford: Clarendon, 1975.

[4] MALKIN, A.YA. AND CHALYKH, A.E., *Diffusion and Viscosity of Polymers: Measurement Techniques*, Moscow: Khimiya, 1979.

[5] VASENIN, R.M., et al. Vysokomol. Soedin., Vol. 7, **1965**, p. 593

[6] BORN, M. AND WOLF, E., *Principles of Optics*, London: Pergamon, 1968.

[7] PRESS, W.H., TEUKOLSKY, S.A., VETTERLING, W.T., FLANNERY, B.P., *Numerical Recipes in C. The Art of Scientific Computing,* Cambridge Univ. Press, 1992.

[8] ASKADSKII, A.A. KONDRASHENKO, V.I., *Computer-Based Materiology of Polymers,* Moscow: Scientific World, Vol. 1, 1999.

[9] MARIOTH, E., et al. Ind. Eng. Chem. Res., Vol. 39, **2000**, p. 4853